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A THERMIONIC EMISSION MODEL FOR THE INITIAL REGIME OF  
SILICON OXIDATION(U) NORTH CAROLINA UNIV AT CHAPEL HILL  
DEPT OF CHEMISTRY E A IRENE ET AL 03 JUN 87 TR-14  
N00014-86-K-0305

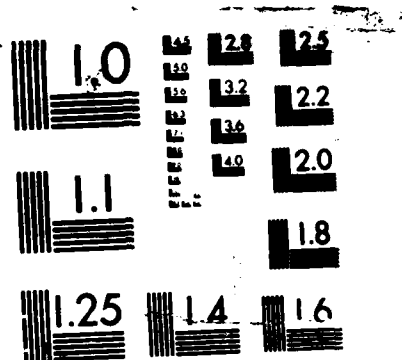
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OFFICE OF NAVAL RESEARCH  
CONTRACT NO. N00014-86-K-0305  
TECHNICAL REPORT NO. 14

Thermionic Emission Model for the Initial Regime of Silicon Oxidation

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in

Applied Physical Letters

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JUN 17 1987  
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# REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #14			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION UNC Chemistry Dept.		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research (Code 413)		
6c. ADDRESS (City, State and ZIP Code) 11-3 Venable Hall 045A Chapel Hill, NC 27514			7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract #N00014-86-K-0305		
8c. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy, Arlington, VA 22217			10. SOURCE OF FUNDING NOS.		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			WORK UNIT NO.		
11. TITLE (Include Security Classification) A THERMIONIC EMISSION MODEL FOR THE INITIAL REGIME OF SILICON OXIDATION					
12. PERSONAL AUTHOR(S) E.A. Irene and E.A. Lewis					
13a. TYPE OF REPORT Interim Technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Yr., Mo., Day) June 3, 1987	
15. PAGE COUNT 16					
16. SUPPLEMENTARY NOTATION Prepared for publication in Applied Physical Letters					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>The very early stage of the thermal oxidation of single crystal Si has been the subject of continual study for the last two decades. In the light of very recent experimental oxidation data on the initial regime, we report that a simple thermionic electron flux from Si into SiO<sub>2</sub> closely agrees with the SiO<sub>2</sub> film growth rate. The importance of electrons for the oxidation kinetics has also been attested to in several recent experimental studies. Thus a consistent model is presented for the initial oxidation regime based on the electron flux as the rate limiting step.</p> <p>silicon dioxide</p>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input checked="" type="checkbox"/> DTIC USERS <input type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson			22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

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Accession For	
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Unannounced	<input type="checkbox"/>
Justification	
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### Abstract

The very early stage of the thermal oxidation of single crystal Si has been the subject of continual study for the last two decades. In the light of very recent experimental oxidation data on the initial regime, we report that a simple thermionic electron flux from Si into  $\text{SiO}_2$  closely agrees with the  $\text{SiO}_2$  film growth rate. The importance of electrons for the oxidation kinetics has also been attested to in several recent experimental studies. Thus a consistent model is presented for the initial oxidation regime based on the electron flux as the rate limiting step.

The kinetics for the formation of  $\text{SiO}_2$  films on Si has received considerable attention both from the technological and scientific viewpoint (see refs. 1-5 and refs. therein). Many models have been proposed (see refs. 1,4,5 and references therein) based on new phenomena incorporated into the Linear-Parabolic, L-P, model proposed in the 1960's(6-8). This latter model considers only the processes of transport of oxidant and reaction of oxidant and silicon in a steady state and as kinetically simple processes. However, a growing body of studies(1,4,5 and references therein) now show that the simple L-P model is inadequate and further elucidation of what was thought to be simple processes is necessary. Of particular relevance are a number of studies on the initial oxidation regime which have implicated the interface reaction as the dominating process(9-17) for  $\text{SiO}_2$  films thinner than 100nm.

The purpose of this letter is to show that a key step in the interface reaction process is the emission of electrons from Si to  $\text{SiO}_2$ . This idea was suggested in a number of earlier studies(14,17-20), but quantification has not been possible because the appropriate experimental oxidation data has only recently become available.

Calculations comparing the maximum diffusion flux of oxygen with oxidant flux obtained from the experimental oxidation rates have shown that transport is not rate limiting below at least 100nm(10,18-20). Random walk calculations and a consideration of the thermodynamic potentials for transport and the interface

reaction further support that the interface reaction must be considered in the Si oxidation process(18-20). A steady state between these two processes likely occurs with the interface reaction having the smaller maximum value. This steady state situation is complex and treated in more detail elsewhere(20).

Recently, there has been substantial experimental evidence supporting the kinetic importance of the interface reaction in the initial regime of oxidation. The very recent extensive oxidation data of Lewis et al.(10,12) using five Si orientations is concordant with previous studies(9,13) that show the oxidation rate order parallels the Si atom areal density for the initial oxidation regime. Perhaps more significant is the new finding that the rates of oxidation are orientation dependent even well beyond 100nm SiO<sub>2</sub> growth(10).

Two recent studies have strongly suggested the importance of the availability of electrons to the oxidation mechanism. The study of photon enhanced oxidation by Young and Tiller(14) shows that there are three regimes of photon energy that enhance the oxidation rate. Photon energies above 3eV show large enhancements of more than ten fold compared with lower energies. The 3eV and higher energy photons likely excite electrons over the Si-SiO<sub>2</sub> barrier. The 5eV and greater energy radiation decomposes O<sub>2</sub> to atomic oxygen with a resulting enhancement compared to the 3eV energies. The recent work by d'Heurle et al.(15) and Frampton et al.(16) shows that different metal silicides, that are oxidized under conditions which preserve the silicide film and form only



SiO<sub>2</sub>, display oxidation rates in the order dictated by the availability of free electrons on the silicide surface. This finding supports previous studies by Cros(17) which strongly suggested that the higher density of electrons at the Fermi level was influential in determining the Si oxidation rate.

The control of the oxidation kinetics at the Si-SiO<sub>2</sub> interface, plus the requirement for electrons enables the following formulation of a new Si oxidation model based on thermionic emission of electrons from Si into SiO<sub>2</sub>. Thermionic emission of electrons in terms of the electron flux, F<sub>e</sub>, is governed by the Richardson-Dushman equation which may be written as:

$$F_e = AT^2 \exp(-\chi_e/kT) \quad (2)$$

where A is the Richardson constant, T is absolute temperature, and  $\chi_e$  is the barrier height which for metals extends from the Fermi energy to vacuum for thermionic emission to vacuum. For the case of emission from Si to SiO<sub>2</sub>, we modify the situation by considering electron emission from levels in Si that have sufficient electrons for the oxidation reaction. From the band diagram in Figure 1, several options are seen for the promotion of an electron from Si to the SiO<sub>2</sub> conduction band. The emission from the densely populated Si valence band requires about 4.25eV, from the intrinsic Fermi level of Si about 3.70eV, and from the Si conduction band about 3.15eV is required.

The model assumes that the electron flux into  $\text{SiO}_2$  is rate limiting and governed by the Richardson equation. We show first that this choice for the rate limiting flux is reasonable, and then the specific mechanism steps are presented. Depicted in Figure 2 are the fluxes now considered. It was previously shown(10,18-20) that the maximum diffusive flux of oxidant,  $F(D)$ , is larger than the experimental flux of  $\text{O}_2$ ,  $F(\text{exp})$ . Before we focus on the assumed rate limiting step,  $F_{\text{ep}}$ , the electron flux to the Si surface,  $F_e$ , must be considered. This flux can be estimated from the relationships:

$$F_e = D_e N_e / L_e \quad (3)$$

$$D_e = \mu_e (kT/e) \quad (4)$$

where  $D_e$  and  $N_e$  are the electron diffusivity and concentration, respectively,  $\mu_e$  is the electron mobility, and  $L_e$  is the distance into the bulk Si away from the oxidized surface. Using literature values for  $\mu_e$  and  $N_e$ , it is found that even at  $L_e$  values greater than  $10^3 \text{ nm}$  the electron flux is  $10^4$  times larger than the oxidation rate. Thus, with the three flux situation in Figure 2, only the electron flux over the barrier,  $F_{\text{ep}}$ , remains for evaluation.

In order to establish that  $F_{\text{ep}}$  is a possible rate limiting flux, the values of  $x_0$  that yield values for  $F_{\text{ep}}$  which are identical to the experimental oxidation flux,  $F(\text{exp})$  are

calculated. The  $\chi_0$  values required for the equivalency of  $F_0$  with  $F(\text{exp})$  are shown in Table 1 for several oxidation temperatures. Several points are made from this Table. First, and most important, is the finding that at all temperatures the calculated value for  $\chi_0$  corresponding to the very initial  $\text{SiO}_2$  growth regime is within about 0.2eV of the barrier of 3.15eV from the bottom of the Si conduction band. While this result seems impressive, it should be remembered that a value of 0.2eV alters the electron flux,  $F_0$ , by about  $10^1$ . The agreement could be physically significant, however, considering that the position of the  $\text{SiO}_2$  band edge has at least tenths of an eV uncertainty at room temperature, and at the higher temperatures is more uncertain. Based on experiments on the Al- $\text{SiO}_2$  interface(22) in which it is observed that the barrier is apparently lowered at elevated temperatures, it is quite likely that the Si- $\text{SiO}_2$  barrier is also lowered at higher temperatures. However, it is also known that the Si band gap decreases at elevated temperatures(21), thereby populating higher levels in the Si conduction band. Thus the precise definition of the band edges is uncertain to at least several tenths of an eV. Next is the result that the (110) orientation, the fastest oxidizing Si surface in the initial regime consistently displays the lowest  $\chi_0$ . It is clear that this difference is forced by the requirement of the equivalence of the fluxes. An independent measurement of the barrier on different orientations would provide confirmation for the proposed model. There is the general result that for all

temperatures and orientations there is an apparent increase in  $\chi$  for the larger film thicknesses. This is most noticeable for the higher oxidation temperatures where, due to experimental difficulties, there is no reliable data available for  $\text{SiO}_2$  less than 5nm. This effect is also likely an artifact due to the growing importance of other kinetically significant processes such as transport of oxidant, film stress or the reduction of the oxidant concentration at the interface.

The question whether there are sufficient electrons in the Si conduction band to permit  $F_{ox}$  to control the rate is answered affirmatively for any temperature above room temperature. At room temperature there is near equivalence at about  $10^{19} \text{ cm}^{-3}$  for both the number of electrons required considering one per  $\text{O}_2$  molecule and actually present. Another question arises from the observation that even at room temperature, a 1nm native oxide grows rapidly on the Si surface and then oxidation is slow up to 2nm where oxidation essentially stops unless impurities are present or the temperature is raised. The question is how does this oxide grow without sufficient electrons (or at least marginally sufficient) and then why does it stop? This problem is understood if we consider that a restricted number of electrons are available in defect states on the Si surface, ie. so called surface states. Such states are known to trap electrons(23), and thus provide a limited source of electrons other than by emission over the barrier (perhaps by a tunneling mechanism for example). In order to form 1nm of  $\text{SiO}_2$  per  $\text{cm}^2$

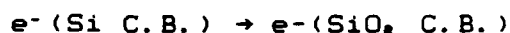
requires about  $2 \times 10^{15}$  electrons at one electron per  $\text{SiO}_2$  molecule. This number is approximately equal to the experimentally determined number of surface states per  $\text{cm}^2$  on a freshly cleaved Si surface(24). Thus an initial native oxide about 1nm thick would have sufficient electrons available to form rapidly and without high temperatures, as is observed. It follows that once the 1nm  $\text{SiO}_2$  forms, the surface states are reduced to below the  $10^{15} \text{ cm}^{-2}$  level, the barrier is formed, and the emission process over the barrier is rate limiting.

With the flux of electrons as the rate limiting step, the oxidation mechanism is envisioned to have the following four main steps with step two being rate limiting:

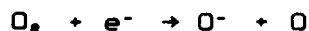
1. In the Si conduction band:



2. At the Si- $\text{SiO}_2$  barrier:



3. In  $\text{SiO}_2$ :



4. The interfacial reaction:



Accordingly, both the formation and reaction of atomic O is important in this mechanism. The electron attachment reaction to  $\text{O}_2$  is not only a favored thermodynamical process, but also the resulting molecular ion,  $\text{O}_2^{\cdot-}$ , has a lower dissociation energy thereby producing more atomic O species(25). The importance of the reaction of atomic oxygen with Si has been discussed by Ghez

and van der Meulen(26) to explain the pressure dependence of the oxidation rate, by Blanc(27) to explain the unusually fast initial oxidation regime and by Irene(28) to explain the curvature of Arrhenius plots of the initial regime rate constant.

With this thermionic model, several perplexing facts about Si oxidation in the very initial oxidation regime become obviated. The observed sensitivity of the oxidation kinetics to impurities and indeed to the cleaning process for the Si wafers(29,30) is understood in the context of recent studies that shows that changes in barrier heights of tenths of an eV are measured for nickel silicides on silicon when interfacial defects and common impurities such as C are present(31). The rapid formation of an initial oxide of about 1nm on Si with the subsequent decrease in rate to low values requiring high temperatures for oxidation to proceed measurably is also explained.

The authors gratefully acknowledge useful discussions with W.A. Tiller and F.M. d'Heurle. This research was supported in part by the Office of Naval Research (ONR).

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### List of Tables

Table 1. The barrier heights,  $\chi_0$ , yielding a thermionic electron flux,  $F_0$ , equal to the experimental  $O_2$  flux,  $F(\text{exp})$ . Data from references 9 and 10.

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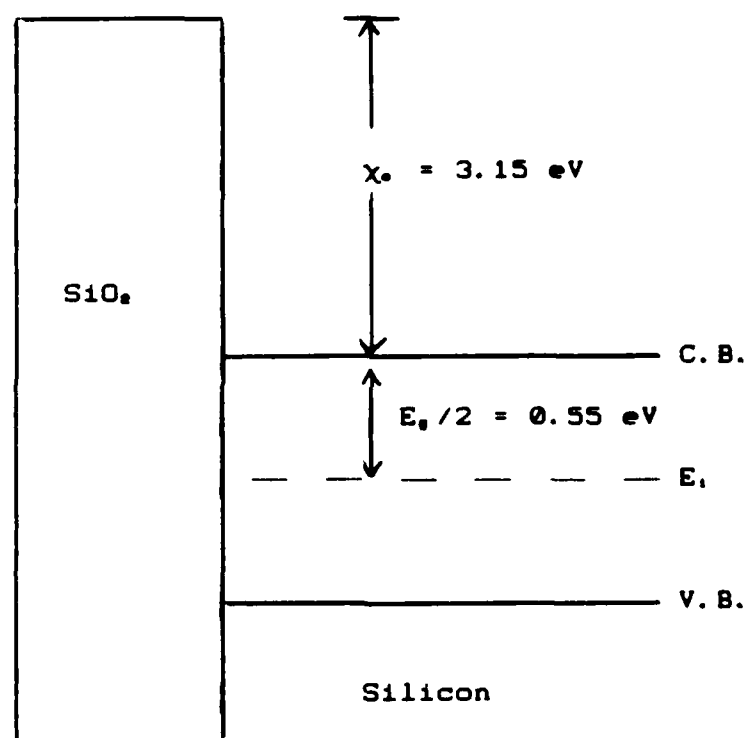
- Figure 1. Energy band diagram for Si-SiO<sub>2</sub>.
- Figure 2. The fluxes for the thermionic emission model:  $F(D)$ , the diffusive flux;  $F_e$ , the electron flux; and  $F_{te}$ , the thermionic emission flux of electrons.

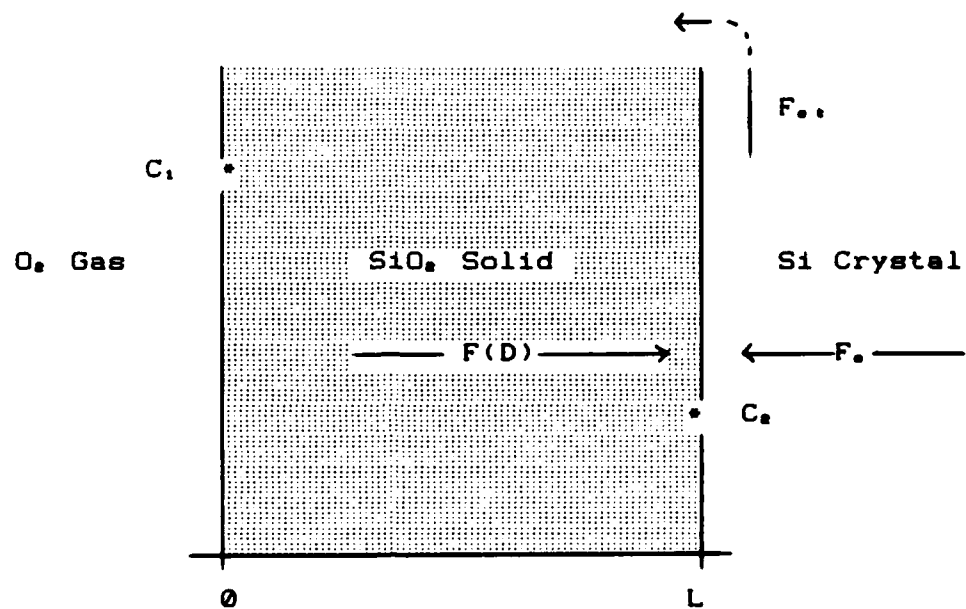
Table 1

Oxidation Temperature (°C)	Si Orientation	Oxidation Rate (nm/min)	SiO <sub>2</sub> Thickness Range (nm)	$\chi$ (eV)
600	(100)	0.0004	2-3	2.87
	(110)	0.0012	2.5-6	2.79
650	(100)	0.014	2.5-7	2.95
	(110)	0.041	2.5-10	2.86
700	(100)	0.014	2.5	2.92
		0.0057	10	3.00
		0.0043	20	3.02
	(110)	0.033	2.5	2.85
		0.014	10	2.92
		0.0094	20	2.96
750	(100)	0.028	5	3.02
		0.024	10	3.03
		0.019	20	3.06
	(110)	0.057	5	2.96
		0.035	10	3.00
		0.024	20	3.04
1000	(100)	1.79	7	3.35
		0.9	20	3.43
		0.27	100	3.56
	(110)	3.45	9	3.28
		1.74	20	3.35
		0.4	100	3.52

# Si-SiO<sub>2</sub> Band Diagram

Vacuum Level





$$F(D) = D(C_1 - C_2) / L(\text{SiO}_2)$$

$$F_s = D_s N_s / L(\text{Si})$$

$$F_{s1} = AT^2 \exp(-\chi_s / kT)$$

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